LIQUID ELECTROLYTE SYSTEMS FOR ADVANCED LITHIUM BATTERIES

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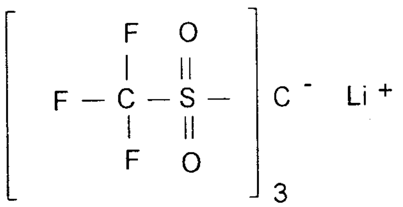
Introduction

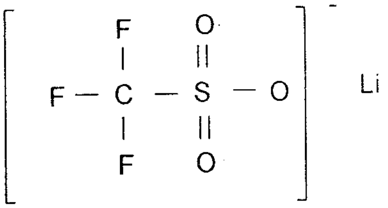
- The selection of the conductive salts, their concentration, the mixture of the solvents and the properties of the single solvents strongly influence the chemical and physical properties of the electrolyte system.

- Therefore the conductivity, viscosity and electrochemical stability of electrolyte mixtures and electrolyte components are systematically investigated. The results depend on temperature, salt concentration and mixture ratios.

- The salts $LiPF_6$, $LiBF_4$, $LiSO_3CF_3$ (Li-triflate) and $LiC(SO_2CF_3)_3$ (Li-methide) are selected for these investigations.



Li-methide



Li-triflate

- The properties of these salts are measured in binary mixtures based on ethylene carbonate (EC) and dimethyl carbonate (DMC).

Conductivity

Comparison of conductivities of the 4 different lithium salts (fig. 1)

In the figures 2-5 the conductivity measurements of the 4 different salts are shown in dependence of temperature and concentration of the salt

a) Relation of molecular weight and concentration

Lithium salt	**MW [g/mol]**	**Conc.** ***at max. conductivity*** **[mol/l]**
$LiBF_4$	93,74	↑ 1,50
$LiPF_6$	151,90	1,00
$LiSO_3CF_3$	156,01	1,00
$LiC(SO_2CF_3)_3$	↓ 418,15	0,75

Tab. 1

b) Influence of the mixture ratios EC:DMC

Conductivities of 0,75 M Li-methide and 1 M LiPF6 electrolytes are determined in variation of the EC:DMC ratios (fig. 6).

Viscosity of Electrolytes

- Fig. 7 shows the viscosity of single solvents, solvent mixture and one electrolyte example.
- In fig. 8 the viscosities of the 4 electrolytes at 1 molar concentrations are compared.
- In the used solvent mixture of EC:DMC the viscosity of electrolytes corresponds to the molecular weight of the added salt.

Electrochemical stability by CV

Measurement conditions:
Working electrode: Pt
Reference and counter electrode: Li
Electrolytes: 1M $LiPF_6$ respectively Li-methide in EC:DMC 50:50 wt%

Results:

- The well known electrolyte $LiPF_6$ in EC:DMC is used as a reference. No significant reduction peaks are seen in the potential range from 0 to 3V. The Li-methide electrolyte is directly compared to the $LiPF_6$ electrolyte in fig. 9 and 10.

Salt	**Oxidation stability 1. cycle**	**Oxidation stability 5. cycle**
$LiPF_6$	5,0V	5,55V
Li-methide	5,3V	5,45V

- Passivation of aluminum by Li-methide at anodic potentials was discussed in literature [1].

- A recently published study gives evidence of the high Li-methide cycling efficiency corresponding to its protecting surface chemistry on lithium [2].

Summary & Conclusions

1. The viscosity of these electrolytes is not directly corresponding to their conductivity.

2. The molecular weight of salts and the conductivity of electrolytes are not in direct correlation.

3. At ambient and higher temperatures conductivity becomes dependent on:

    - the kind of conducting salt (fig. 1)

CONDUCTIVITY

$$\xrightarrow{\hspace{12cm}}$$

$LiSO_3CF_3$ $LiBF_4$ $LiC(SO_2CF_3)_3$ $LiPF_6$

- the concentration of the salt. Its optimum concentration depends on the molecular weight: the higher the molecular weight of the salt the lower its concentration (tab. 1)

- the ratio of the used EC:DMC binary mixture (fig. 6)

4. Li-methide provides an excellent salt for low temperature battery applications because of its ability to lower the solidification of liquid electrolytes. The suppression of the freezing point (compare fig. 2 and fig. 5) could be explained by the large charge delocalization of this anion which reduces ion-pairing to keep the Li-methide salt in solution [1].

5. The electrochemical stability of the 2 conducting salts $LiPF_6$ and Li-methide are comparable by CV.

Acknowledgement

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Notes

1. C.W. Walker jr., J.D. Cox, M. Salomon , J. Electrochem. Soc. **143** (1996) L80
2. D. Aurbach, O. Chusid, I. Weissman, P. Dan, Electrochimica Acta **41** (1996) 747

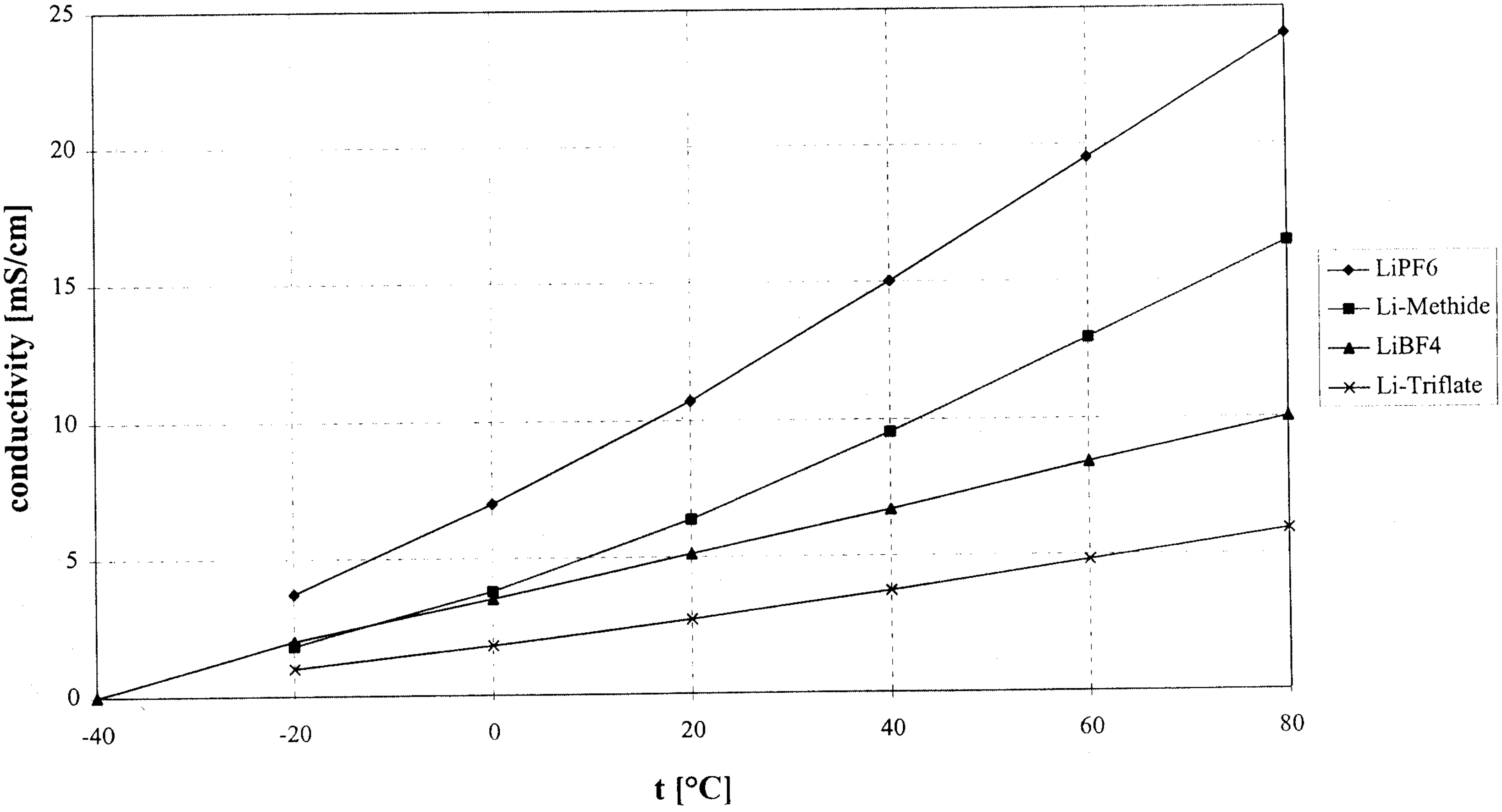

Fig. 1: Comparison of conductivity of 4 different Li-salts
(1 M Li-salt in EC:DMC 50:50 wt%)

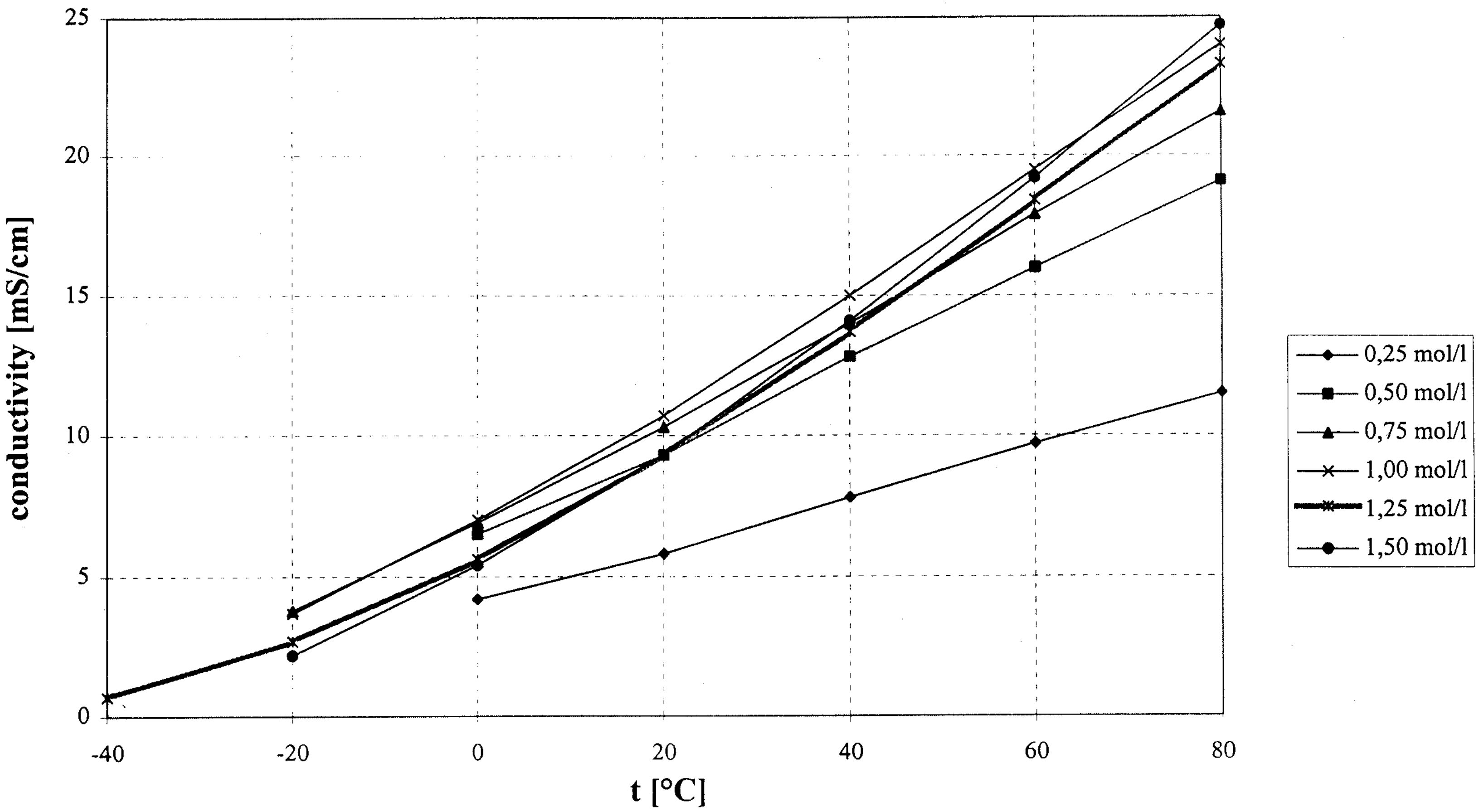

Fig. 2: LiPF6 in EC:DMC (50:50 wt%)

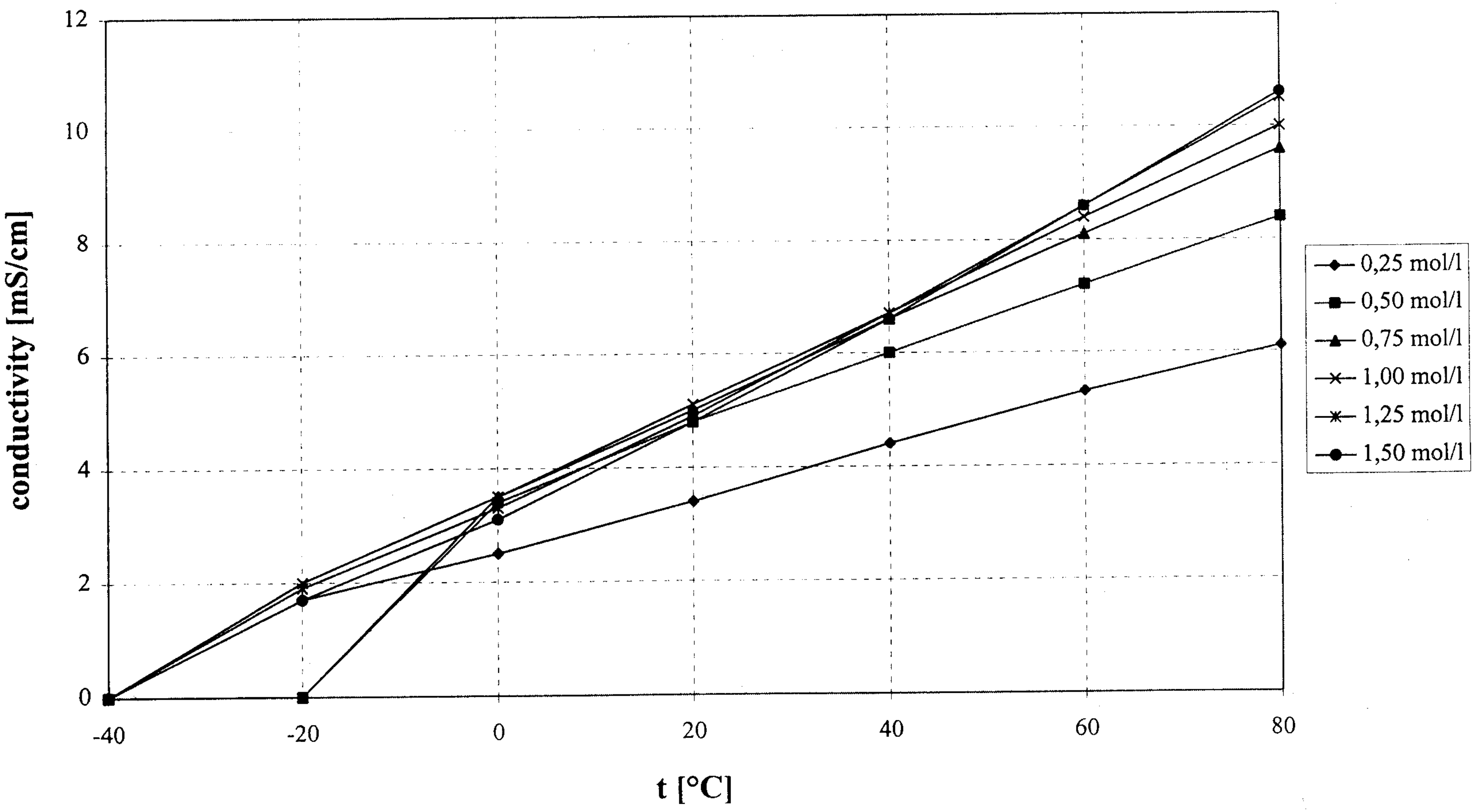

Fig. 3: LiBF4 in EC:DMC (50:50 wt%)

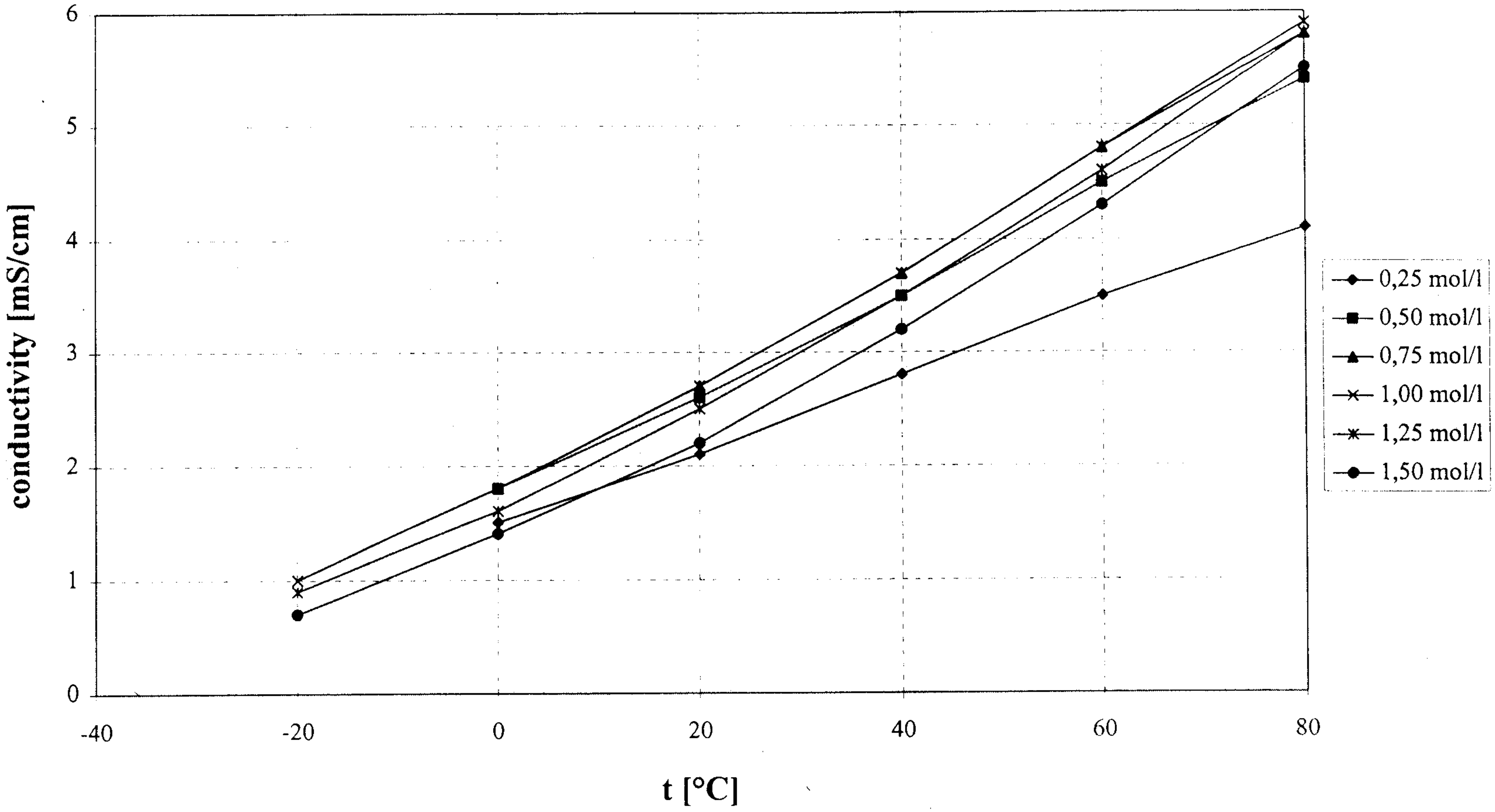

Fig. 4: Li-triflate in EC:DMC (50:50 wt%)

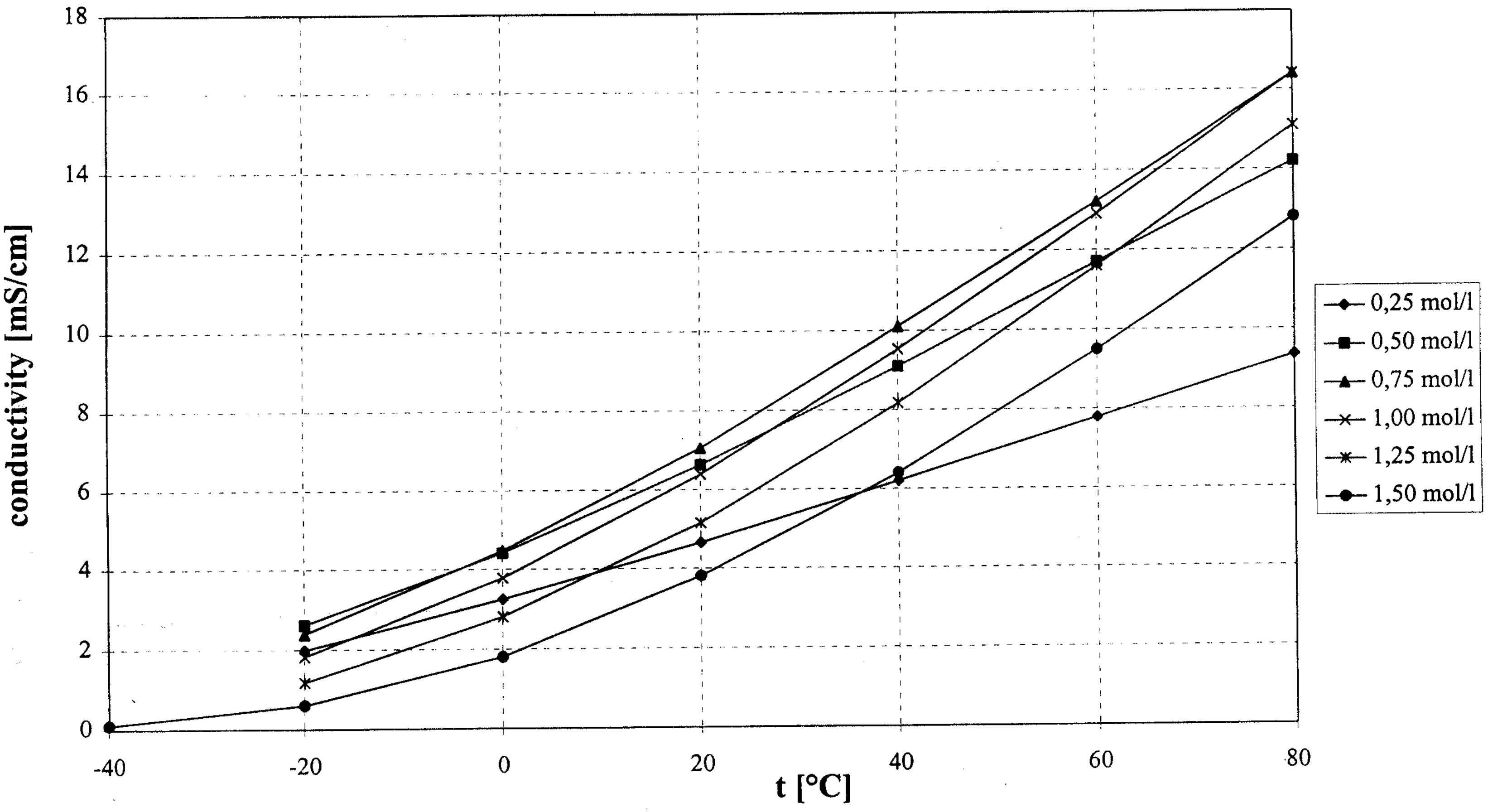

Fig. 5: Li-methide in EC:DMC (50:50 wt%)

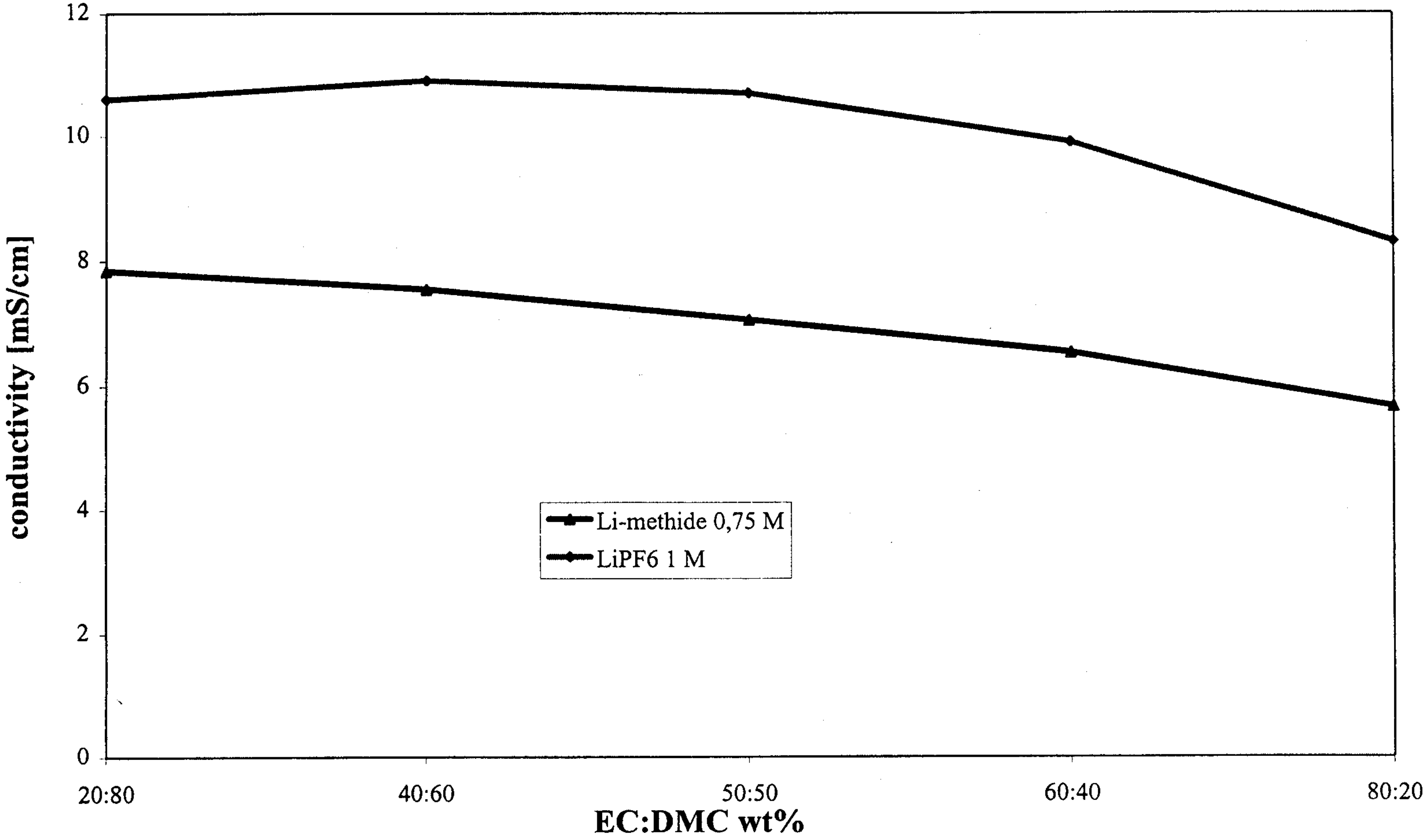

Fig. 6: LiPF6 and Li-methide in EC:DMC, 20°C

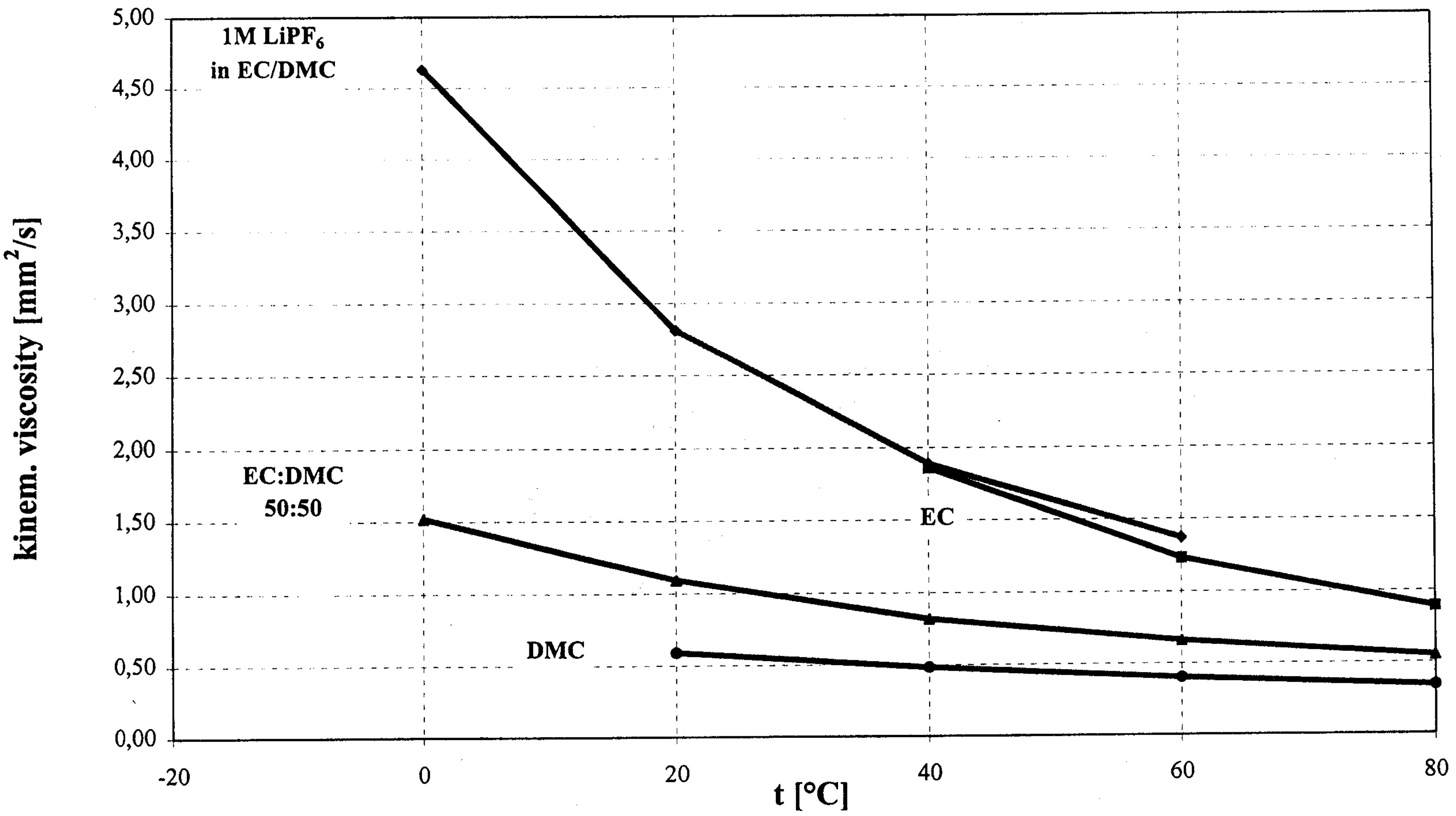

Fig. 7: Viscosity solvent - solvent mixture - electrolyte

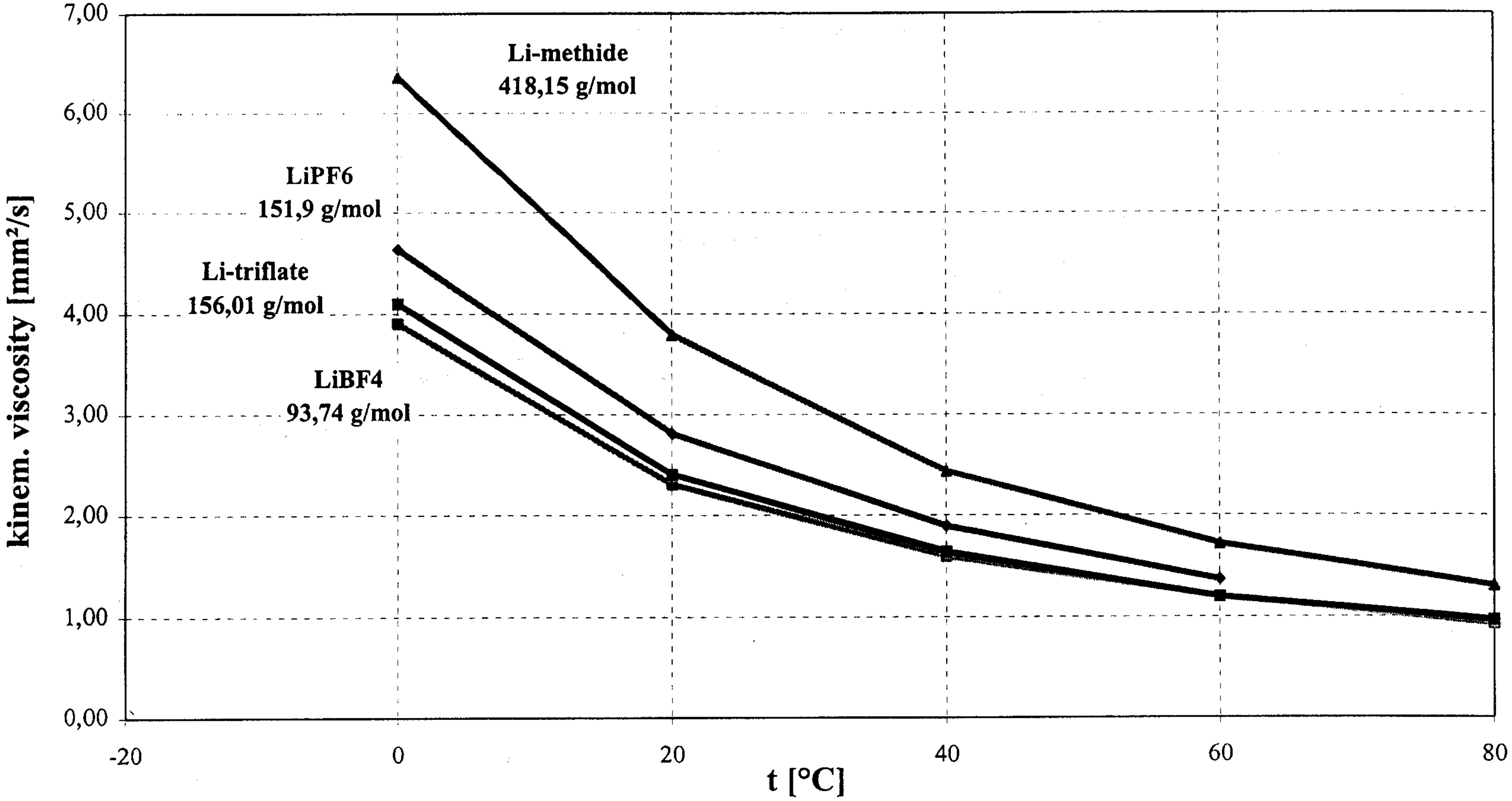

Fig. 8: Viscosity of 1M Li-salts in EC:DMC (50:50 wt%)

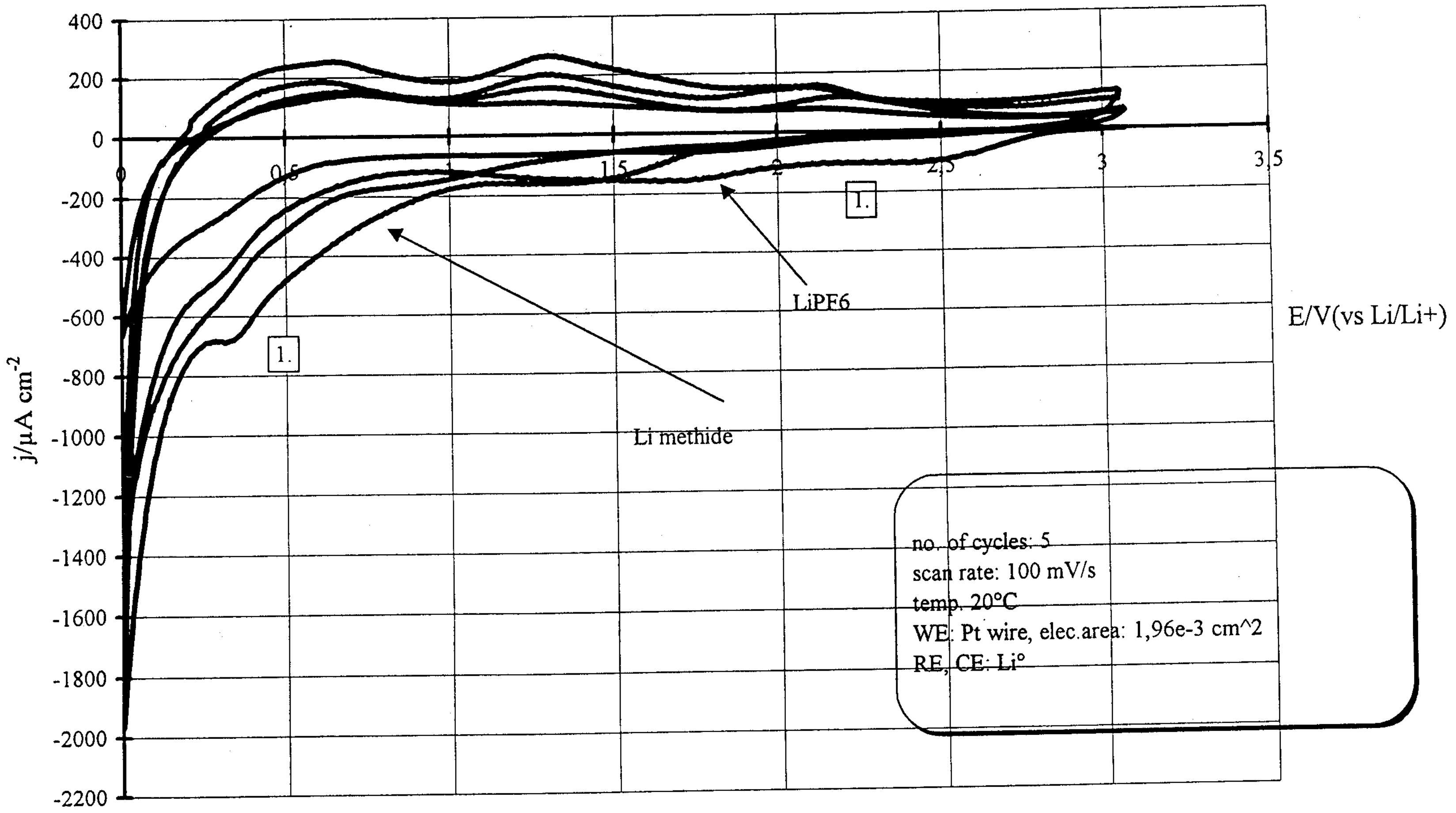

Fig 9: CV: low potential range 0V - OCV (~3V)
in EC:DMC (50:50 by vol%)

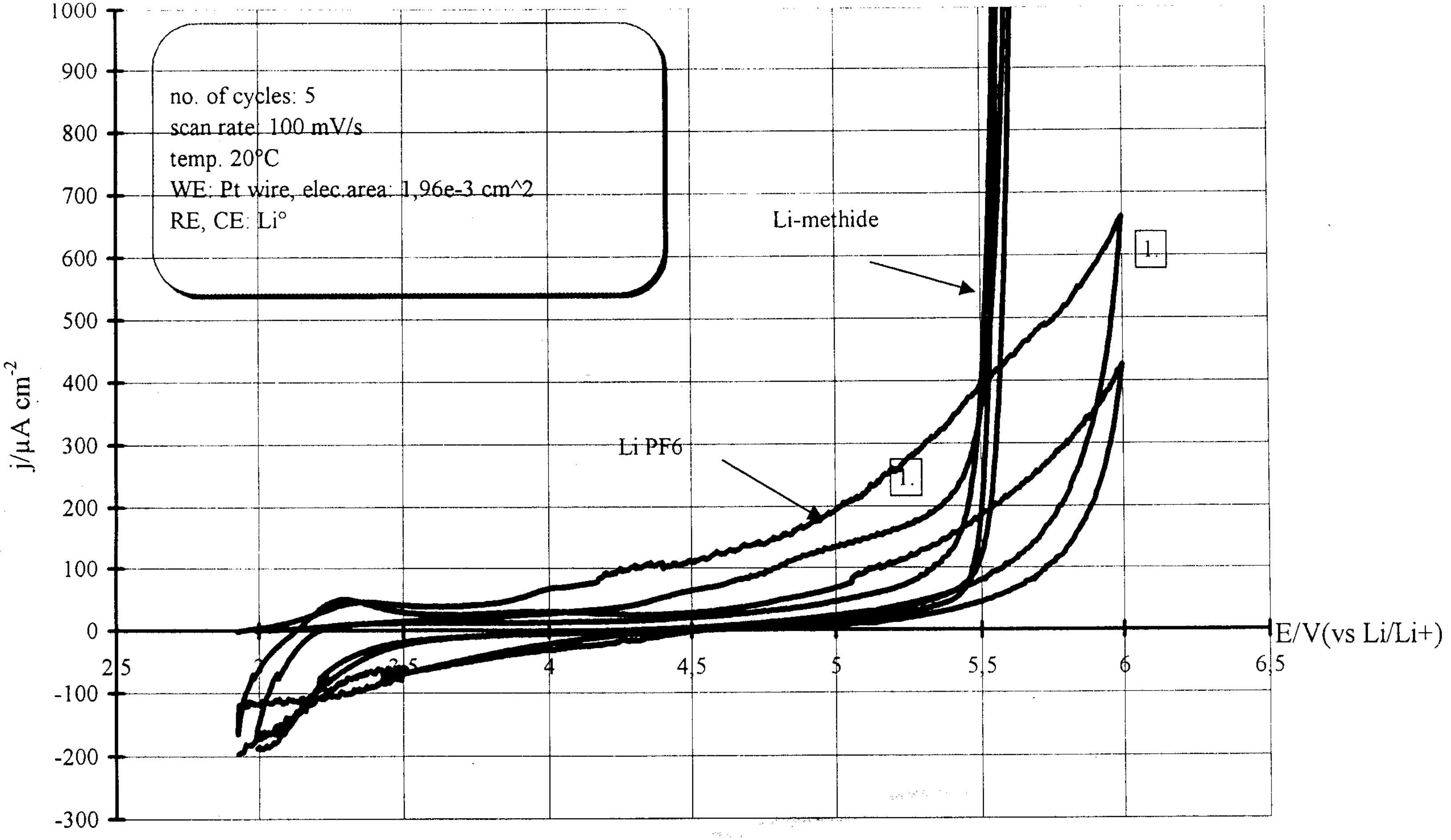

Fig 10: CV: high potential range OCV (~3V)- 6V in EC:DMC (50:50 by vol%)